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(54) Title: HIGH DRAWDOWN EXTRUSION PROCESS
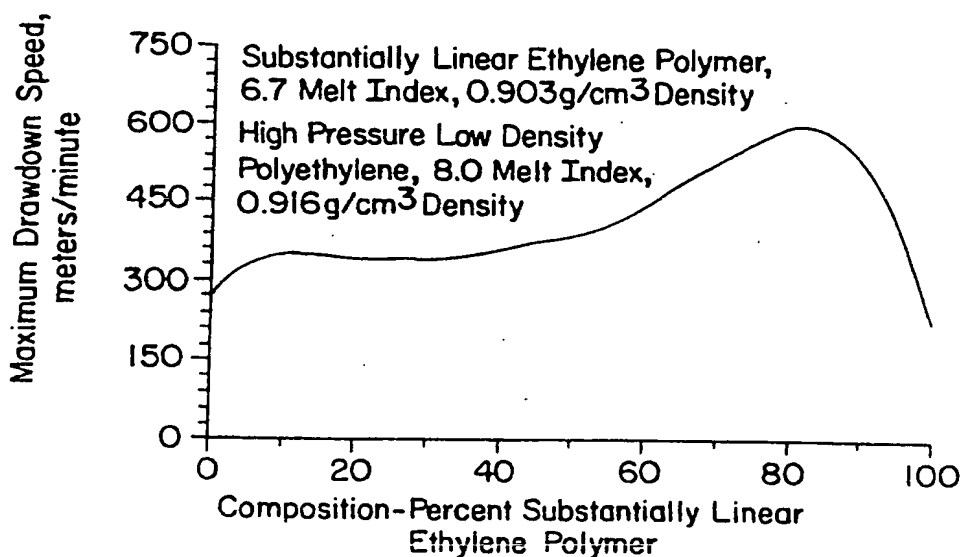
(57) Abstract

A process for extruding a thermoplastic composition at higher drawdown rates with less neck-in and greater resistance to draw resonance as well as processes for extrusion coating a substrate and for making an extrusion-cast film are disclosed. The thermoplastic composition is made of at least one substantially linear ethylene polymer used alone or in combination with at least one high-pressure ethylene polymer and/or with at least one heterogeneous linear olefin polymer.

HIGH DRAWDOWN EXTRUSION PROCESS

This invention pertains to an improved olefin extrusion composition, a
5   process for extrusion coating a substrate or article, and a process for
making an extrusion cast film. More particularly, this invention pertains
to extrusion coating and extrusion cast film compositions with higher
drawdown rates, lower neck-in and higher resistance to draw resonance.
The extrusion compositions contain at least one substantially linear
10 ethylene polymer as the thermoplastic component and may beneficially
include at least one high-pressure ethylene polymer and/or at least one
linear ethylene polymer.

It is known that low density polyethylene (LDPE) made by high-pressure
15 polymerization of ethylene with free-radical initiators as well as
heterogeneous linear low density polyethylene (LLDPE) and ultra low
density polyethylene (ULDPE) made by the copolymerization of ethylene and
α-olefins with Ziegler coordination (transition metal) catalysts at low
to medium pressures can be used to extrusion coat substrates such as paper
20 board as well as used to prepare extrusion cast film for applications such
as disposable diapers and food packaging. However, although LDPE
generally exhibits excellent extrusion processability and high extrusion
drawdown rates, LDPE extrusion coatings and cast films lack sufficient
abuse resistance and toughness for many applications. Conversely, while
25 LLDPE and ULDPE extrusion coatings and cast films offer improved abuse
resistance and toughness properties, these ethylene a-olefin polymers can
not be extruded or drawn at high take-off rates and they are known to
exhibit relatively poor extrusion processability.
        The ultimate extrusion drawdown rate of known linear ethylene
30 polymers is limited (at otherwise practicable extrusion line speeds) by
the onset of a melt flow instability phenomena known as draw resonance
rather than being limited by melt tension breaks due to "strain hardening"
which occurs at higher line speeds and are typical for LDPE and other
highly branched high pressure ethylene polymers such as, for example,
35 ethylene-acrylic acid (EAA) copolymers and ethylene vinyl acetate (EVA)
copolymers.

"Draw resonance" or "melt surging" occurs in LLDPE, ULDPE and other linear polymers such as high density polyethylene (HDPE), polypropylene and polyester during processing that involves rapid drawing or pulling of the melt such as extrusion coating, extrusion cast film

5   fabrication, profile extrusion and fine denier fiber spinning. Also, the onset or occurrence of draw resonance is unmistakable.

The patent teachings of Kurtz et al. in US Patent 4,339,507 and Lucchesi et al. in US patent 4,486,377 describe draw resonance as a sustained random and/or periodic oscillation, variation or pulsation of

10   the polymer melt with respect to the velocity and cross-sectional area of a melt drawing process that occurs between the die and the take-off position when the boundary conditions are a fixed velocity at the die and a fixed velocity at the take-off position. Draw resonance occurs when the draw ratio (that is, the melt velocity at take-off divided by the melt

15   velocity instantaneous at the die exit often approximated by dividing the reciprocal of the final polymer thickness by the reciprocal of the thickness of the melt instantaneous at the die exit) exceeds a polymer specific critical value. Draw resonance is a melt flow instability that is manifested as irregularities in the final coating, film or fiber

20   dimensions and often produce widely variable thicknesses and widths. When line speeds significantly exceed the speed of onset, draw resonance can cause web or filament breaks and thereby shut down the entire drawing or converting process.

Given the various differences and intricacies that can exist

25   between different extrusion equipment, relative resistance to draw resonance is often expressed in terms of critical draw ratio, and for conventional linear ethylene polymers, maximum stable draw ratios have been found to be less than 10:1, although draw ratios greater than 20:1 are needed for most commercial drawing operations.

30   "Drawdown" is defined herein to mean stretching or elongating a molten polymer extrudate (web or filament) in the machine direction and occasionally (simultaneously to a lesser degree) also in the transverse direction.

"Melt tension" which is also referred to in the relevant art

35   as "melt strength" is defined and quantified herein to mean the stress or force (as applied by a wind-up drum equipped with a strain cell) required

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to draw a molten extrudate at some specified rate above its melting point
as it passes through the die of a standard plastometer such as the one
described in ASTM D1238-E. Melt tension values, which are reported herein
in grams, are determined at 190 C using a 2.16 kg weight and a 30 rpm
5   wind-up rate. In general, for conventional linear and high pressure
ethylene polymers, melt tension tends to increase with increased molecular
weight, or with broadening of the molecular weight distribution and/or
with increased melt flow ratios.

"Neck-in" which is influenced by extrudate swelling and, to
10   lesser degree, by surface tension effects is defined herein as the
difference between the die width and the web width at the take-off
position. Measured neck-in values (at constant output) will remain
constant or decrease as the drawdown rate increases, and, in general, it
is well known that for conventional ethylene polymers neck-in values
15   increase as molecular weight decreases and/or as the molecular weight
distribution narrows.

"Take-off position" is defined herein to mean the contact
point (either the top or bottom) of a roller device that draws or pulls
the molten extrudate down from its initial thickness instantaneous at the
20   die exit to its final thickness. The roller device can be a nip roll,
rubber roll, a chill roll, combinations thereof, or the like constructed
from, for example, metal or rubber with various surfaces such as polished,
matte or embossed finishes; all of which can to varying degrees affect
the onset of draw resonance.

25   A variety of potential solutions have been disclosed to
address the neck-in and/or draw resonance tendencies of linear polymers.
Many of these solutions are equipment related and others primarily relate
to modification of the properties of the linear polymers by forming
polymer blends with highly branched high pressure ethylene polymers such
30   as, for example, low density polyethylene. Thompson in US Patent
4,348,346 is an example of equipment related attempts to address neck-in
and draw resonance. Thompson describes a secondary injection of polymer
melt streams into the primary die at the edges of the primary web stream
is described to reduce neck-in and provide improved edge bead control.

35   An equipment modification solution specific to retarding the
onset of draw resonance is provided by Cancio et al. in US Patent

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4,668,463 and US Patent 4,626,574 where locating a draw roller not more than 6 inches (15.2 cm) from the die provides a short air/draw gap and reduced draw resonance. Luchessi et al. in US Patent 4,486,377, teaches the use of a fluid medium, for example, nitrogen, carbon monoxide or air, directed against the molten web prior to the take-off position as a viable method of retarding draw resonance. Similarly, Kurtz et al. in US Patent 4,608,221 discloses that draw resonance can be mitigated by the utilization of a tensioning device with a friction free surface in a "rapid cooling zone" between the die and the take-off position.

Conversely, as another equipment modification example for alleviating or reducing draw resonance, Chaing in US Patent 4,859,379 discloses radiant heating of the molten web prior to a chill roll take-off position.

Examples of modified linear polymer compositions exhibiting reduced draw resonance include US Patent 4,378,451 (Edwards), which discloses high flow rate compositions based on degraded propylene polymers blended with low density polyethylene. A similar example is provided by Werkman et al. in US Patent 3,247,290 wherein thermally degraded (visbroken) high density polyethylene is blended with low density polyethylene to prepare high drawdown extrusion coating compositions. Another linear polymer blend example involving low density polyethylene is disclosed by Kurtz et al. in US Patent 4,339,507 where high pressure LDPE at 20 to 98 weight percent in combination with heterogeneous conventional LLDPE is taught to provide extrusion coating compositions with improved running rates.

An example of compositions that reduce draw resonance without the inclusion of a polymer degradation step and/or blending with a branched high pressure ethylene polymer is taught by Dohrer et al. in US Patent 4,780,264 where LLDPE with melt flow ratios less than 8.3 (that is, utilizing molecular weight distributions even more narrow than typically employed) were found to allow surprisingly fast line speeds in extrusion coating and extrusion casting. However, predictably, these materials also exhibit higher neck-in and/or poor extrusion processability (for example, higher extruder amperage).

In spite of the various advances, there is still a need for avoiding draw resonance and high neck-in problems when extruding known

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linear olefin polymer compositions at high extrusion line speeds. More
particularly, there is also a need for extrusion coating and extrusion-
casting materials that allow even higher line speeds and better extrusion
processability than the lower melt flow ratio linear olefin polymers
5   taught by Dohrer et al. in US Patent 4,780,264 and the polymer blends
described by Kurtz et al. in US Patent 4,339,507. It is also desirable to
avoid mechanical or equipment modifications that are designed to alter the
drawing process itself as a means of attaining greater resistance draw
resonance and lower neck-in. Additionally, to a lesser extent, there is
10   also a desire to avoid the extra detail involved in providing
appropriately degraded polymers as separately described by Werkman et al.
and Edwards. As described hereinafter, the present invention
substantially fills such desires and needs by providing compositions
comprising at least one substantially linear ethylene polymer. However,
15   if cast film or extrusion coating equipment modifications are already
installed, and/or if blending with thermally degraded polymers is desired,
or if the use of linear olefin polymers with lower melt flow ratios is
desired, the present invention can still be employed to good advantage and
the combined or synergistic benefits of the present invention and known
20   solutions can also be realized.

          In accordance with the present invention, we have discovered a
new and improved:
          Process for extrusion coating a substrate or for making a cast
25   film with a thermoplastic composition, comprising the steps of:
              (i)   feeding a thermoplastic composition into at least
                     one extruder,
              (ii)   melting and mixing the thermoplastic composition   to
                     form at least one uniform molten polymer stream,
30   (iii) extruding the molten polymer stream through a die to
                     form a primary web,
     the improvement comprising:
              (i)   operating said extruder at line speeds greater than 152
                     meters/minute, and either

(a)   drawing down said web onto said substrate to
thereby coat said substrate with at least one layer of
said thermoplastic composition, or

(b)   cooling and drawing down said web onto a take-off
device to make said film with at least one layer
of said thermoplastic composition,

(ii)   transporting or collecting said coated substrate or
said film for subsequent use, and

(iii)   using as said thermoplastic composition:

(I)   from 10 to 100 percent by weight of at least one
substantially linear ethylene polymer
characterized as having:

(a)   a melt flow ratio, I_{10}/I_2, $\geq$ 5.63,

(b)   a molecular weight distribution,
M_w/M_n, defined by the equation:
$M_w/M_n \leq (I_{10}/I_2) - 4.63$,

(c)   a critical shear rate at the onset of surface
melt fracture of at least 50 percent greater
than the critical shear rate at the onset of
surface melt fracture of a linear olefin
polymer having the same I_2 and M_w/M_n, and

(d)   a single melting peak as determined using
differential scanning calorimetry; and

(II)   from 0 to 90 percent by weight of at least
one polymer selected from the group
consisting of a heterogeneous linear ethylene
polymer and high pressure ethylene polymer.

With the present invention, one obtains reduced neck-in, higher drawdown
rates, and greater resistance to draw resonance than obtainable with
heterogeneous linear ethylene polymers.

DESCRIPTION OF THE DRAWINGS

Figure 1 is a plot showing the maximum drawdown rate as a
function of weight percent of a 6.7 Melt Index substantially linear
ethylene polymer blended with a 8 Melt Index high pressure low density
polyethylene.

Figure 2 is a plot of the zero shear melt viscosity as a function of weight percent high pressure low density polyethylene for two blends comprising substantially linear ethylene polymers with a high pressure low density polyethylene polymer and one blend comprising a

5   conventional heterogeneous linear low density polyethylene polymer with a high pressure low density polyethylene polymer.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

10   Substantially Linear Ethylene Polymers: The substantially linear ethylene polymers (either homopolymers or interpolymers) used in the present invention are a unique class of compounds that are further defined in issued US Patent 5,272,236 and US Patent 5,278,272.

Substantially linear ethylene homopolymers and interpolymers

15   are a truly unique class of ethylene polymers. They differ substantially from the class of conventional homogeneously branched linear ethylene/a-olefin copolymers described by Elston in US Patent 3,645,992, and moreover, they are not in the same class as conventional heterogeneous Ziegler polymerized linear ethylene polymers (for example, ultra low

20   density polyethylene, linear low density polyethylene or high density polyethylene made, for example, using the technique disclosed by Anderson et al. in US Patent 4,076,698, and utilized by Dohrer et al. as described in US Patent 4,780,264), nor are they in the same class as free-radical initiated highly branched high pressure low density ethylene homopolymer

25   and ethylene interpolymers such as, for example, ethylene-acrylic acid (EAA) copolymers and ethylene-vinyl acetate (EVA) copolymers.

The substantially linear ethylene homopolymers and interpolymers useful in this invention have excellent processability, even though they have relatively narrow molecular weight distributions and

30   exhibit improved resistance to draw resonance such that cast films and extrusion coatings with uniform dimensions can be prepared at higher extrusion line speeds. Surprisingly, in light of disclosures by Dohrer and Niemann (US Patent 4,780,264 and ANTEC Proceedings 1989, "Resistance to Draw Resonance of Linear Low Density Polyethylene Through Improved

35   Resin Design", page 28-30), the melt flow ratio (I_{10}/I_2) of the substantially linear ethylene homopolymers or interpolymers can be varied

widely and essentially independently of the polydispersity index (that is, the molecular weight distribution, M_w/M_n). More particularly, this behavior is also a contradistinction to the linear ethylene/α-olefin copolymers described by Elston in US Patent 3,645,992 and to the

5   heterogeneous conventional Ziegler polymerized linear polyethylene copolymers having rheological properties such that as the polydispersity index increases, the I_{10}/I_2 value also increases.

The term "homogeneously branched" when applied to ethylene/a-olefin copolymers is defined herein to mean that (1) the α-olefin

10   comonomer is randomly distributed within a given molecule, and (2) substantially all of the copolymer molecules have the same ethylene-to-comonomer ratio. When the term "homogeneously branched" is applied to both ethylene homopolymers and copolymers, it is defined herein to mean that (1) the polymer is characterized by a narrow short chain branching

15   distribution where the short chain branching index (defined herein below) is greater than 30 percent, more preferably greater than 50 percent, and (2) the polymer essentially lacks a measurable high density (crystalline) polymer fraction as measured by known fractionation techniques such as, for example, a method that involves polymer fractional elutions as a

20   function of temperature.

The term "high pressure" or "highly branched" is defined herein to mean that the polymer is partly or entirely homopolymerized or interpolymerized in autoclave or tubular reactors at pressures above 14,500 psi (100 MPa) with the use of free-radical initiators.

25   The term "interpolymer" is used herein to indicate a copolymer, or a terpolymer, or the like, where, at least one other comonomer is polymerized with ethylene to make the interpolymer.

The term "polymer" is used herein to indicate homopolymer and/or interpolymer, where ethylene is polymerized alone or with at least

30   one other comonomer.

The term "thermoplastic" is used herein to indicate polymers or polymer compositions that are substantially thermally extrudable or deformable albeit relatively aggressive conditions may be required.

The term "substantially linear" means that the polymer

35   backbone is substituted with 0.01 long chain branch/1000 carbons to 3 long chain branches/1000 carbons, more preferably from 0.01 long chain

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branches/1000 carbons to 1 long chain branch/1000 carbons, and especially from 0.05 long chain branch/1000 carbons to 1 long chain branch/1000 carbons.

The term "long chain branching" is defined herein as a chain
5   length of at least about 6 carbons, above which the length cannot be distinguished using ^{13}C nuclear magnetic resonance spectroscopy, yet the long chain branch can be about the same length as the length of the polymer back-bone.

Long chain branching is determined by using ^{13}C nuclear
10   magnetic resonance (NMR) spectroscopy and is quantified using the method described by Randall (Rev. Macromol. Chem. Phys., C29, V. 2&3, p. 285-297).

The substantially linear homopolymers for use in the extrusion compositions, films, coatings and processes of the present invention are
15   polymers of ethylene involving no additional monomer or comonomer although at least one chain transfer agent may be employed to affect specific polymer molecular characteristics. The substantially linear ethylene interpolymers for use in the present invention have a single melting peak at densities less than 0.91 grams/cm^3 , as opposed to conventional
20   heterogeneous Ziegler polymerized polymers which have two or melting points as determined using differential scanning calorimetry (DSC). Also, the substantially linear ethylene polymers of the present invention are interpolymers of ethylene with at least one C_3-C_{20} α-olefin and/or C_4-C_{18} diolefin. Copolymers of ethylene and an a-olefin of C_3-C_{20} carbon atoms
25   are especially preferred.

Suitable unsaturated comonomers useful for polymerizing with ethylene include, for example, ethylenically unsaturated monomers, conjugated or non-conjugated dienes, polyenes, etc. Examples of such comonomers include C_3-C_{20} α-olefins as propylene, isobutylene, 1-butene,
30   1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, 1-decene, and the like. Preferred comonomers include propylene, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene, and 1-octene is especially preferred. Other suitable monomers include styrene, halo- or alkyl-substituted styrenes, tetrafluoroethylene, vinylbenzocyclobutane, 1,4-hexadiene, 1,7-
35   octadiene, and cycloalkenes, for example, cyclopentene, cyclohexene and cyclooctene.

The density of the substantially linear ethylene interpolymers or homopolymers (as measured in accordance with ASTM D-792) for use in the present invention is generally greater than about 0.85 grams/cubic centimeter (g/cm^3), especially from 0.86 g/cm^3 to 0.96 g/cm^3, more preferably, from 0.87 g/cm^3 to 0.955 g/cm^3, and most preferably, from 0.88 to 0.95 g/cm^3.

The molecular weight of the substantially linear ethylene interpolymers or homopolymers is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190 C/2.16 kilogram (kg), formerly known as "Condition E" and also known as I_2. Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear. The melt index for the substantially linear ethylene interpolymers and homopolymers useful herein is generally from 0.01 gram/10 minutes (g/10 min.) to 40 g/10 min., preferably from 0.1 g/10 min. to 35 g/10 min., and especially from 1 g/10 min. to 20 g/10 min.

Other measurements useful in characterizing the molecular weight of substantially linear ethylene interpolymers and homopolymers involve melt index determinations with higher weights, such as, for common example, ASTM D-1238, Condition 190 C/10 kg (formerly known as "Condition N" and also known as I_{10}). "Melt flow ratio" is defined herein as the ratio of a higher weight melt index determination to a lower weight determination, and for measured I_{10} and the I_2 melt index values, the melt flow ratio is conveniently designated as I_{10}/I_2.

Unlike heterogeneous conventional linear polymers which possess no substantial long chain branching, for the substantially linear ethylene interpolymers and homopolymers used to prepare the extrusion compositions, cast films and extrusion coatings of the present invention, the melt flow ratio actually indicates the degree of long chain branching, that is, the higher the I_{10}/I_2 melt flow ratio, the more long chain branching in the polymer. The I_{10}/I_2 ratio of the substantially linear ethylene interpolymers and homopolymers is preferably at least about 5.63, and especially from 5.63 to 18, and most especially from 6 to 15.

The "rheological processing index" (PI) which is defined herein as the apparent viscosity in kpoise of a polymer measured by a gas extrusion rheometer (GER), can also be used to distinguish the

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substantially linear ethylene polymers of this invention. The gas
extrusion rheometer is described by M. Shida, R.N. Shroff and L.V. Cancio
in _Polymer Engineering Science_, Vol. 17, No. 11, p. 770 (1977), and in
"Rheometers for Molten Plastics" by John Dealy, published by Van Nostrand

5   Reinhold Co. (1982) on pp. 97-99, both publications of which are
incorporated by reference herein in their entirety. GER experiments are
performed at a temperature of 190°C, at nitrogen pressures between 250 to
5500 psig (17-379 bars) using about a 7.54 cm diameter, 20:1 L/D die with
an entrance angle of 180°. For the substantially linear ethylene polymers

10   described herein, the PI is the apparent viscosity (in kpoise) of a
material measured by GER at an apparent shear stress of 2.15×10^6
dyne/cm^2. The unique substantially linear ethylene interpolymers and
homopolymers described herein preferably have a PI in the range of 0.01
kpoise to 50 kpoise, preferably about 15 kpoise or less. The unique

15   substantially linear ethylene interpolymers and homopolymers described
herein have a PI less than or equal to about 70 percent of the PI of a
comparative linear ethylene polymer (either a Ziegler polymerized polymer
or a linear uniformly branched polymer as described by Elston in US Patent
3,645,992) at about the same I_2 and M_w/M_n.

20   To more fully characterize the rheological behavior of the
unique substantially linear ethylene polymers, S. Lai and G.W. Knight
recently introduced (_ANTEC '93 Proceedings_, INSITE™ Technology
Polyolefins (ITP) - New Rules in the Structure/Rheology Relationship of
Ethylene a-Olefin Copolymers, New Orleans, La., May 1993) another

25   rheological measurement, the Dow Rheology Index (DRI), which expresses a
polymer's "normalized relaxation time as the result of long chain
branching." DRI ranges from 0 for polymers which do not have any
measurable long chain branching (for example, Tafmer™ and Exact™
products) to about 15 and is independent of melt index. In general, for

30   low to medium pressure ethylene polymers (particularly at lower densities)
DRI provides improved correlations to melt elasticity and high shear
flowability relative to correlations of the same attempted with melt flow
ratios, and for the substantially linear ethylene polymers of this
invention, DRI is preferably at least about 0.1, and especially at least

35   about 0.5, and most especially at least 0.8. DRI can be calculated from
the equation:

$$DRI = (3652879 * \tau_0^{1.00649}/\eta_0 - 1)/10$$

where τ_0 is the characteristic relaxation time of the material and η_0 is the zero shear viscosity of the material. Both τ_0 and η_0 are the "best fit" values to the Cross equation, that is

$$\eta/\eta_0 = 1/(1 + (\dot{\gamma} * \tau_0)^{1-n})$$

where **n** is the power law index of the material, and η and γ are the measured viscosity and shear rate, respectively. Baseline determination of viscosity and shear rate data are obtained using a Rheometric Mechanical Spectrometer (RMS-800) under dynamic sweep mode from 0.1 to 100 radians/second at 160 C and a Gas Extrusion Rheometer (GER) at extrusion pressures from 1,000 psi to 5,000 psi (corresponding shear stress from 0.086 to 0.43 MPa) using a 7.54 centimeter diameter, 20:1 L/D die at 190 C. Specific material determinations can be performed from 140 to 190 C as required to accommodate melt index variations.

For the substantially linear ethylene polymers of this invention, DRI relates linearly to draw ratio in accordance with the equation:

$$\text{Critical Draw Ratio} = 9.0641 + 29.264 * DRI.$$

For the substantially linear ethylene polymers of the present invention, the molecular interrelationship between melt index, melt tension and maximum draw ratio before the onset of draw resonance is expressed by the following equation:

$$\text{Critical Draw Ratio} = a * MT - b * MI - c * MT^2 + d * MI^2 + e * MT * MI$$

where,
a is a coefficient from 39 to 60, and especially from 45 to 53; b is a coefficient from 7 to 11, and especially from 8

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to 10.5;   c is a coefficient from 33 to 46, and especially
from 36 to 43;   d is a coefficient from 0.5 to 0.9, and
especially from 0.55 to 0.85;   e is a coefficient from 13 to
24, and especially from 16 to 21;   MT is Melt Tension
5   determined at 190 C as described above;   and MI is Melt Index
determined in accordance with ASTM D1238 Condition 190 C/2.16
kg.

In addition to the onset of draw resonance and various
10   rheological characterizations, ethylene polymers can also be distinguished
by melt flow consequences that are manifested as solid state surface
defects.   Unlike draw resonance which is observed during drawing and
pertains to irregularities in the extrudate dimension, an apparent shear
stress versus apparent shear rate plot is used to identify the "melt
15   fracture" phenomena which pertains to surface irregularities.   According
to Ramamurthy in the Journal of Rheology, 30(2), 337-357, 1986, above a
certain critical shear rate (in contrast to a critical draw rate for the
draw resonance phenomena), the observed extrudate irregularities may be
broadly classified into two main types: surface melt fracture and gross
20   melt fracture.

Surface melt fracture occurs under apparently steady flow
conditions and ranges in detail from loss of specular film gloss to the
more severe form of "sharkskin."   In this disclosure, the onset of surface
melt fracture (OSMF) is characterized at the beginning of losing extrudate
25   gloss at which the surface roughness of the extrudate can only be detected
by 40x magnification.   The critical shear rate at the onset of surface
melt fracture for the substantially linear ethylene interpolymers and
homopolymers is at least 50 percent greater than the critical shear rate
at the onset of surface melt fracture of a comparative linear ethylene
30   polymer (either a Ziegler polymerized polymer or a linear homogeneously
branched polymer as described by Elston in US Patent 3,645,992) having
about the same I_2 and M_w/M_n.

Gross melt fracture occurs at unsteady extrusion flow
conditions, and ranges in detail from regular (alternating rough and
35   smooth, helical, etc.) to random distortions.   For commercial
acceptability, (for example, in cast films and bags therefrom), surface

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defects should be minimal, if not absent, for good film/coating quality
and properties. The critical shear stress at the onset of gross melt
fracture for the substantially linear ethylene interpolymers and
homopolymers used in the present invention is greater than about 4×10^6

5   dynes/cm^2. The critical shear rate at the onset of surface melt fracture
(OSMF) and the onset of gross melt fracture (OGMF) will be used herein
based on the changes of surface roughness and configurations of the
extrudates extruded by a GER.

The distribution of comonomer branches for the substantially

10   linear ethylene interpolymers and homopolymers is characterized by its
SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition
Distribution Branch Index) and is defined as the weight percent of the
polymer molecules having a comonomer content within 50 percent of the
median total molar comonomer content. The CDBI of a polymer is readily

15   calculated from data obtained from techniques known in the art, such as,
for example, temperature rising elution fractionation (abbreviated herein
as "TREF") as described, for example, by Wild et al., Journal of Polymer
Science, Poly. Phys. Ed., Vol. 20, p. 441 (1982), or in US Patent
4,798,081. The SCBDI or CDBI for the substantially linear interpolymers

20   and homopolymers of the present invention is preferably greater than about
30 percent, especially greater than about 50 percent.

The substantially linear ethylene interpolymers and
homopolymers used in this invention essentially lack a measurable "high
density" fraction as measured by the TREF technique. The substantially

25   linear interpolymers and copolymers do not contain a polymer fraction with
a degree of branching less than or equal to 2 methyls/1000 carbons. The
"high density polymer fraction" can also be described as a polymer
fraction with a degree of branching less than about 2 methyls/1000
carbons. Among other benefits, the lack of high density polymer fraction

30   permits improved coating smoothness, printability, optical properties as
well as enhanced film/coating flexibility and elasticity.

The substantially linear ethylene interpolymers and homopolymers are
analyzed by gel permeation chromatography (GPC) on a Waters 150 high

35   temperature chromatographic unit equipped with differential refractometer
and three columns of mixed porosity. The columns are supplied by Polymer

Laboratories and are commonly packed with pore sizes of 10^3, 10^4, 10^5 and 10^6Å. The solvent is 1,2,4-trichlorobenzene, from which 0.3 percent by weight solutions of the samples are prepared for injection. The flow rate is 1.0 milliliters/minute and the operating temperature is 140 C with a
5   100-microliter injection size.

The molecular weight determination with respect to the polymer backbone is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are
10   determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Ward in _Journal of Polymer Science_, Polymer Letters, Vol. 6, p. 621, 1968, incorporated herein by reference) to derive the following equation:

15
$$M_{polyethylene} = a * (M_{polystyrene})^b.$$

In this equation, $a = 0.4316$ and $b = 1.0$. Weight average molecular weight, M_w, is calculated in the usual manner according to the following formula: $M_w = R\ w_i * M_i$, where w_i and M_i are the weight fraction
20   and molecular weight, respectively, of the ith fraction eluting from the GPC column.

For the substantially linear ethylene interpolymers and homopolymers used in the present invention, the M_w/M_n is preferably from 1.5 to 8, and especially from 1.7 to 6.5.

25

Single site polymerization catalysts, for example, the monocyclo-pentadienyl transition metal olefin polymerization catalysts described by Canich in US Patent 5,026,798 or by Canich in US Patent 5,055,438 or constrained geometry catalysts for example, as described by Stevens et al.
30   in US Patent 5,064,802, can be used to polymerize the substantially linear interpolymers and copolymers, so long as the catalysts are used consistent with the methods described in US Patent 5,272,236 and US Patent 5,278,272. Such polymerization methods are also described in PCT/US 92/08812 (filed October 15, 1992), the disclosure of which is incorporated herein by

reference. However, the substantially linear ethylene interpolymers and

homopolymers are preferably made by using suitable constrained geometry

catalysts, especially constrained geometry catalysts as disclosed in US

Application Serial Nos.: 545,403, filed July 3, 1990; 758,654, filed

5   September 12, 1991; 758,660, filed September 12, 1991; and 720,041, filed

June 24, 1991.

Suitable cocatalysts for use herein include but are not

limited to, for example, polymeric or oligomeric aluminoxanes, especially

methyl aluminoxane or modified methyl aluminoxane (made, for example, as

10   described in US Patent 5,041,584, US Patent 4,544,762, US Patent

5,015,749, and/or US Patent 5,041,585) as well as inert, compatible, non-

coordinating, ion forming compounds. Preferred cocatalysts are inert,

non-coordinating, boron compounds.

15   The polymerization conditions for manufacturing the substantially linear

ethylene homopolymers and interpolymers of the present invention are

preferably those useful in the solution polymerization process, although

the application of the present invention is not limited thereto. Slurry

and gas phase polymerization processes are also useful, provided the

20   proper catalysts and polymerization conditions are employed. To

polymerize the substantially linear interpolymers and copolymers useful in

the invention, the single site and constrained geometry catalysts

mentioned earlier can be used, but for substantially linear ethylene

polymers the polymerization process should be operated such that the

25   substantially linear polymers are formed. That is, not all polymerization

conditions inherently make the substantially linear ethylene polymers,

even when the same catalysts are used.

For example, in one embodiment of a polymerization process

useful in making the novel substantially linear ethylene polymers, a

30   continuous process is used, as opposed to a batch process.

Preferably, for substantially linear ethylene polymers, the

polymerization is performed in a continuous solution polymerization

process. Generally, manipulation of I_{10}/I_2 while holding M_w/M_n relatively

low for producing the substantially linear ethylene polymers using

35   constrained geometry catalyst technology described herein is a function of

reactor temperature and/or ethylene concentration. Reduced ethylene

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concentration and higher temperature generally produces higher I_{10}/I_2.
Generally, as the ethylene concentration of the reactor decreases, the
polymer concentration increases. For the novel substantially linear
ethylene interpolymers and homopolymers, the polymer concentration for a
5 continuous solution polymerization process is preferably above about 5
weight percent of the reactor contents, especially above about 6 weight
percent of the reactor contents. Generally, the polymerization
temperature of the continuous process, using constrained geometry catalyst
technology, is from 20 C to 250 C. If a narrow molecular weight
10 distribution polymer (M_w/M_n of from 1.5 to 2.5) having a higher I_{10}/I_2
ratio (for example I_{10}/I_2 of about 7 or more, preferably at least about 8,
especially at least about 9) is desired, the ethylene concentration in the
reactor is preferably not more than about 8 percent by weight of the
reactor contents, especially not more than about 6 percent by weight of
15 the reactor contents, and most especially not more than about 4 percent by
weight of the reactor contents.

Multiple reactor polymerization processes can also be used in
making the substantially linear olefin interpolymers and homopolymers of
the present invention, such as those processes disclosed in copending US
20 applications serial number 07/815,716 filed December 30, 1991 and serial
number 08/010,958 filed January 29, 1993, and in US Patent 3,914,342. The
multiple reactors can be operated in series or in parallel or a
combination thereof, with at least one constrained geometry catalyst
employed in at least one of the reactors.

25

Additives such as antioxidants (for example, hindered phenolics such as
Irganox® 1010 or Irganox® 1076 supplied by Ciba Geigy), phosphites (for
example, Irgafos® 168 also supplied by Ciba Geigy), cling additives (for
example, PIB), Standostab PEPQ™ (supplied by Sandoz), pigments,
30 colorants, and fillers can also be included in the interpolymers and
copolymers of the present invention, to the extent that they do not
interfere with the improved draw resonance resistance discovered by
Applicants. The extrusion coatings and films may also contain additives
to enhance antiblocking and coefficient of friction characteristics
35 including, but not limited to, untreated and treated silicon dioxide,
talc, calcium carbonate, and clay, as well as primary, secondary and

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substituted fatty acid amides, chill roll release agents, silicone coatings, etc. Other additives may also be added to enhance the anti-fogging characteristics of, for example, transparent cast films, as described, for example, by Niemann in US Patent 4,486,552. Still other

5   additives, such as quaternary ammonium compounds alone or in combination with ethylene-acrylic acid (EAA) copolymers or other functional polymers, may also be added to enhance the antistatic characteristics of coatings and films of this invention and allow, for example, the packaging of electronically sensitive goods.

10   The substantially linear ethylene polymers used to prepare the compositions and products of the present invention can be blended with linear ethylene polymers and/or high pressure ethylene polymers, or used as the only resinous polymer component whether the resultant film or coating to be used is a monolayer or multilayer construction. Still other

15   polymers can also be blended with the substantially linear ethylene interpolymers or homopolymers to modify processing, film strength, heat seal, or adhesion characteristics.

Some useful materials for blending with substantially linear ethylene interpolymers and homopolymers include, for example, but are not

20   limited to, low density ethylene polymer such as high pressure low density ethylene homopolymer (LDPE), ethylene-vinyl acetate copolymer (EVA), ethylene-carboxylic acid copolymers and ethylene acrylate copolymers as well as olefin polymers produced at low to medium pressures such as polybutylene (PB) and ethylene/α-olefin polymers which includes high

25   density polyethylene, medium density polyethylene, polypropylene, ethylene-propylene interpolymers, linear low density polyethylene (LLDPE) and ultra low density polyethylene, as well as graft-modified polymers, and combinations thereof including I_{10}/I_2, MWD, and/or comonomer combinations.

30   Suitable high pressure ethylene interpolymers include ethylene interpolymerized with at least one α,β-ethylenically unsaturated comonomers (for example, acrylic acid, methacrylic acid and vinyl acetate) as described by McKinney et al. in US Patent 4,599,392. Preferred high pressure ethylene interpolymers comprise from 0.1 to 55 total weight

35   percent comonomer, and more preferably from 1 to 35 total weight percent comonomer, and most preferably from 2 to 28 total weight percent

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comonomer, and can be chemically and/or physically modified by any known technique such as, for example, by ionomerization and extrusion grafting.

However, preferred polymer blends comprise at least one substantially linear ethylene polymer, and preferably the substantially
5 linear ethylene interpolymer or homopolymer comprises at least about 5 percent of the blend composition, more preferably at least about 10 percent of the blend composition.

For the multilayer coatings and films of the present invention, any layer and any number of layers can comprise at least one
10 substantially linear ethylene polymer. However, highly preferably, though, for multilayer film and coating constructions, outer layers (alternatively referred to in the art as "skin layers" or "surface layers") and sealant layers would comprise at least one substantially linear ethylene interpolymer and/or homopolymer.

15 The blend compositions of this invention can be prepared by any suitable means known in the art including tumble dry-blending, melt blending via compound or side-arm extrusion, multiple reactor polymerizations or the like as well as combinations thereof. Also, the multilayer constructions of this invention can be prepared by any means
20 known including coextrusion, laminations and combinations thereof. Moreover, compositions of this invention can be employed in coextrusion operations where a higher drawdown material is used to essentially "carry" one or more lower drawdown materials.

The blended and non-blended compositions of this invention, whether
25 of monolayer or multilayer construction, can be used to coat various polar and nonpolar substrates including for example, but not limited to, paper products, metals, ceramics, glass and various polymers, particularly other polyolefins, and combinations thereof.

30 EXAMPLES

The following examples illustrate some of the particular embodiments of the present invention, but the following should not be construed to mean the invention is limited to the particular embodiments shown. Also, practitioners of these arts will appreciate that the maximum
35 line speeds attainable with one type of extruder or coater will not

necessarily be the same as the speeds attainable with another and the same equipment arrangement should be used for meaningful comparisons.

EXAMPLES 1 - 6

5   In the following Examples 1-6, Table 1 summarizes the polymers used in an extrusion coating evaluation. The coating equipment consisted of a two-extruder Black Clawson coextrusion coating line with a 3-1/2 inch (8.9 cm) diameter primary extruder with a 30:1 L/D and a 2-1/2 inch (6.4 cm) diameter secondary extruder with a 24:1 L/D. A 76 cm slot die was
10   attached and deckled to 69 cm with a 20 mil die gap and a 6 inch (15.2 cm) air/draw gap. The targeted extrusion temperature and screw speed for all extrusion coating examples was 610 F (316 C) and 90 rpm, respectively, unless otherwise noted. Molten webs were drawn down to continuous 50 lb. Kraft paper as well as to slip-sheets of aluminum and oriented
15   polypropylene.

Table 1

Sample	Polymer Type	Melt Index (g/10 min.)	Density (g/cc)	Melt Flow Ratio (I_{10}/I_2)	M_w/M_n
A	SLEP	4.5	0.902	7.4	2.15
B	SLEP	4.7	0.910	8.0	2.28
C	SLEP	9.4	0.910	7.5	2.28
D	SLEP	8.1	0.913	6.7	ND
E*	LINEAR	4.0	0.904	7.9	ND
F*	LINEAR	5.4	0.911	7.6	3.4

20   *Not an example of the present invention; provided for comparative purposes only.
SLEP = substantially linear ethylene polymer prepared by the interpolymerization of ethylene and 1-octene.
LINEAR = heterogeneous conventional ultra low density polyethylene prepared by the interpolymerization of
     ethylene and 1-octene as described in USP 4,076,698 and 4,780,264.
ND = not determined.

25

          Samples A-F were evaluated on the above described Black Clawson coextrusion line. The evaluation involved systematically increasing the take-off speed while maintaining a constant screw speed (90 rpm). The line speed where the onset of draw resonance (that is, web
30   began to oscillate) was initially observed, was taken as the ultimate or maximum drawdown rate. The drawdown rate, neck-in measured at a 440 fpm

(134 mpm) line speed for a 1 mil coating thickness and the output rate at
ultimate drawdown are summarized in Table 2 for these samples.

Table 2

Extrusion Coating Results on Draw Resonance and Neck-In

Example	Sample	Drawdown Rate[†] ft/min. (mpm)	Neck-In at 134 mpm / 1 Mil (cm)	Output (kg/hr/hp)
1	A	600 (183)	21	3.2
2	B	650 (198)	21	3.4
3	C	780 (238)	21	3.9
4	D	570 (174)	24	3.2
5*	E	350 (107)	**	2.9
6*	F	440 (134)	23	ND

[†] Drawdown rate = take-off speed at which dimensional irregularities are observed to initially occur.
* Not an example of the present invention; provided for comparative purposes.
**Draw resonance onset at 107 mpm, could not achieve 134 mpm to produce a uniform 1 mil coating and obtain comparative neck-in measurements.
ND = not determined.

As can be observed from the data in Table 2, relative to
heterogeneous conventional linear ethylene polymers, extrusion coating
compositions comprising substantially linear ethylene polymers allow
greater resistance to draw resonance whereby higher extrusion line speeds
are attainable. Surprisingly, in contradistinction to Dohrer et al. in US
Patent 4,780,264 and to the blends described by Kurtz et al. in US Patent
4,608,221, the substantially linear polymers show higher comparative
drawdown rates even at higher melt flow ratios. Table 1 also shows that
substantially linear polymers exhibit less neck-in than heterogeneous
conventional linear polymers, even at appreciably higher melt indices, and
these unique polymers also provide higher extruder pumping rates (as
measured as higher specific outputs) which is indicative of more
efficient, improved processability.

SAMPLES G-K

Table 3 shows the polymers used (Sample G - K) for an
extrusion cast embossed evaluation where the extrusion equipment consisted
of a three-extruder cast coextrusion film line with a 20/60/20 feedblock

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design and a slot die. The extruder diameters were 2-1/2, 3-1/2 and 2
inches (6.4, 8.9 and 5.1 cm), respectively, and the die width measured 76
cm with a 20-mil manual die gap. The evaluation involved a primary chill
roll with either a chrome polished finish (4-5 rms. surface roughness) or
a matte finish (32 rms. surface roughness), and a secondary chill roll
with a chrome polished finish (4-5 rms. surface roughness). The line was
also equipped with a beta thickness gauge, a nip roll with a silicon-based
rubber cover, a squeegee roll and a recirculating water trough system.
Table 4 shows the extrusion cast line conditions that are held constant
for these polymer evaluations.

Table 3

**Polymer Descriptions for
Extrusion Casting Evaluation**

Sample	Polymer Type	Melt Index (g/10 min)	Density (g/cc)	Melt Flow Ratio (I_{10}/I_2)	Melt Tension (grams)
G	SLEP	2.5	0.935	8.8	1.04
H	SLEP	2.4	0.934	11.4	1.46
I*	LINEAR	2.4	0.934	7.4	0.65
J*	LINEAR	4.0	0.941	6.7	0.41
K*	LDPE	2.0	0.922	10.5	3.8

*Not an example of the present invention when used alone.
SLEP = substantially linear ethylene polymer prepared by the interpolymerization of ethylene and 1-octene.
LINEAR = heterogeneous conventional linear low density polyethylene prepared by the interpolymerization
    of ethylene and 1-octene as described in USP 4,076,698 and USP 4,780,264.
LDPE = traditional high pressure low density polyethylene.

Table 4

Constant Conditions for Extrusion Casting Evaluation	
Melt Temperature, C	274
Nip Roll Height, cm	29
Draw Gap, cm	18
Final Film Thickness, mils	1
Chill Roll Temperature, C	21-27
Nip Roll Temperature, C	27
Water Bath Temperature, C	27-35

The onset of extrusion casting draw resonance as defined as
5   maximum drawdown rate was determined by incrementally increasing the line
speed (take-off rate) while concurrently increasing the screw speed to
maintain a constant film thickness at 1 mil until definitive dimension
fluctuations were observed for each polymer. The onset of extrusion cast
draw resonance was also indicated by minimum uniform film thickness or
10   maximum downgaugability. Maximum downgaugability was determined by
increasing line speed at a constant extrusion output rate for each
polymer. Neck-in was determined by measuring the difference between the
die width and the width of the web at the primary chill roll. Table 5
illustrates the evaluation results for the onset of draw resonance by both
15   maximum drawdown rate and downgaugability as well as the extrusion output
at maximum drawdown for each polymer evaluated. Table 5 also includes
results for Inventive Example 12 which is 70/30 weight percent blend of
comparative sample J and Inventive Sample H, respectively.

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Table 5

Extrusion Casting Evaluation

Example	Sample	Maximum Drawdown Rate (meters/min.)	Maximum Downgaugability † (mils)	Neck-In 91 mpm/1 Mil (cm)	Output at Max Drawdown (kg/hr)
7	G	174	0.82	23	200
8	H	>300	<0.76	20	>315
9*	I	53	1.83	ND	<68
10*	J	127	1.06	27	113
11*	K	>300	ND	ND	ND
12ᵃ	L	>152	ND	ND	ND

*Not an example of the present invention; provided for comparative purposes only.
†Total extruder output constant at approximately 138 kg/hr.
ND = not determined.
ᵃAmple quantities were not available to fully determine maximum drawdown rate and neck-in.

Table 5 shows that the unique substantially linear ethylene polymers of this invention allow significant advantages and/or improvements in drawdown rates, downgaugability, neck-in and output in comparison to heterogeneous conventional linear ethylene polymers. Also, contrary to the disclosure by Dohrer et al. (US Patent 4,780,264), the substantially linear ethylene polymer sample (Sample H) with the highest melt flow ratio and highest melt tension exhibits line speeds comparable to low density polyethylene.

EXAMPLES 7 - 12: Film Properties

Table 6 shows that extrusion casting compositions comprising a substantially linear ethylene polymer allow a superior balance of cast film abuse properties and toughness over low density polyethylene at 1.0 mil film thickness. With few exceptions, Table 6 indicates compositions involving a substantially linear ethylene polymer generally provide at least 30 percent better abuse resistance properties (that is, yield strength, toughness, tear resistance and dart impact resistance) relative to comparative low density polyethylene cast film. Given the higher density of the substantially linear ethylene polymer compositions (0.934 g/cm³ versus 0.922 g/cm³ for the comparative LDPE sample), the superior abuse resistance and toughness properties are surprising. Ethylene polymers typically show improved mechanical and abuse resistance properties at lower densities. This relationship is especially true for ethylene/a-olefin copolymers where higher comonomer levels provide lower

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densities and superior toughness. In general, higher density ethylene

polymers, and more particularly, medium density (that is, 0.93 g/cm³ -

0.945 g/cm³) polymers with 1 percent secant moduli above 30,000 psi (207

MPa), are required in cast embossed applications that demand improved

5 convertibility or machineability, that is, the ability for the film to

move and/or be handled smoothly as it passes from one converting or

constructing operation to the next until the final desired product is

produced.

10

Table 6

Extrusion Cast Film
Property Comparisons

Example	Sample	Line Speed for 1 mil film (m/min.)	Yield Strength[†] (MD+TD)/2 (MPa)	Toughness[†] (MD+TD)/2 MJ/m³	TD Tear[††] Resistance (grams)	Dart Impact[†††] (grams)
7	G	91	11.2	84.4	118	55
8	H	152	10.8	62.5	198	38
9*	I	30	9.8	85.6	206	66
10*	J	91	12.7	92.2	92	45
11*	K (LDPE)	152	7.8	60.0	124	34
12	L	152	11.8	78.6	181	45

*Not an example of the present invention; provided for comparative purposes only.

15   Constant extrusion conditions: 18 cm draw gap, 274 C melt temperature for all three extruders, 3.4 bars nip pressure, 27 C nip roll temperature, 21-27 C chill roll temperature, and 27-35 C water bath temp.

[†]Tensile yield strength and toughness are determined in accordance with ASTM D882 where toughness is taken as the integration of the area under the stress/strain curve.

[††]Elmendorf tear resistance is determined in accordance with ASTM D1922; only transverse direction (TD)

20   resistance is reported since it's most important for cast film applications such as disposable diapers as described by Roberts et al. in ANTEC Proceedings '85, pp. 104-7 and by Lucchesi et al., in Plastics Engineering, May 1985, pp. 87-90, the disclosures of both of which are incorporated herein by reference.

[†††]Dart impact is determined in accordance with ASTM D1709 Method A.

25   EXAMPLES 7- 9:   Extrusion Processability

Another evaluation was conducted to further quantify the

superior processability of the unique compositions of the present

invention. Inventive samples G and H and comparative sample I, all with

similar melt indices and polymer densities, were extrusion casted at a

30   constant output rate (that is, approximately 138 kg/hour). The

corresponding amperages and extrusion pressures for each extruder are

listed in Table 7.

Table 7

Extrusion Casting
Processibility Evaluation

Example	7	8	9
	Inventive Sample G	Inventive Sample H	Comparative* Sample I
Screw Speed (rpm)			
6.4 cm Extruder	15.2	16.5	15.6
8.9 cm Extruder	44.7	49.5	45.6
5.1 cm Extruder	33.4	36.8	34.2
Extruder Amperage			
6.4 cm Extruder	16	14	21
8.9 cm Extruder	87	68	108
5.1 cm Extruder	12	11	15
Extruder Pressure (MPa)			
6.4 cm Extruder	11.4	9.0	15.0
8.9 cm Extruder	14.1	10.8	17.9
5.1 cm Extruder	9.2	7.5	12.8

*Not an example of the present invention; provided for comparative purposes only.
Constant extrusion conditions: 18 cm air/draw gap, 274 C melt temperature for all three extruders, 3.4 bars nip pressure, 27 C nip roll temperature, 21-27 C chill roll temperature., and 27-35 C water bath temperature.

As Table 7 shows, compositions of this invention exhibit the significantly lower amperages and extrusion pressures which is indicative of more efficient processibility, that is, lower energy consumption for the same output.

EXAMPLES 13 - 20

In another evaluation, Inventive Samples A, B and C, as well as two other substantially linear ethylene polymers (Inventive Samples M and N) were tumble dry-blended at a 82/18 ratio with a traditional high pressure low density polyethylene to prepare extrusion coating compositions. The compositions were evaluated for the onset of draw resonance on the Black Clawson extrusion coater described above. The Black Clawson coater was operated substantially as indicated above in Example 1 and Table 8 shows the polymer descriptions for Inventive Sample M and N as well as for the LDPE blend component material. Table 9 shows

resultant melt index, drawdown, neck-in and output performance for these various extrusion compositions as well as two additional inventive compositions involving two high pressure ethylene copolymers, that is, an ethylene-acrylic acid (EAA) copolymer and an ethylene-methyl acrylate (EMA) copolymer. Like the coating operation, the drawdown, neck-in and output determinations were performed substantially as indicated for Examples 1-6.

Table 8

Sample	Polymer Type	Melt Index (g/10 min.)	Density (g/cc)	Melt Flow Ratio (I_{10}/I_2)	M_w/M_n
M	SLEP	6.7	0.903	7.4	2.12
N	SLEP	28.0	0.898	6.3	2.23
O*	LDPE	7.9	0.916	ND	7.85
P*	LDPE	4.2	0.923	ND	ND

*Not an example of the present invention when used alone.
SLEP = substantially linear ethylene polymer prepared by the interpolymerization of ethylene and 1-octene.
LDPE = traditional high pressure low density polyethylene.
ND = not determined.

Table 9

Extrusion Coating
Blend
Compositions

Example	Base Polymer (Sample #)	High Pressure Ethylene Polymer (18 percent by wt.)	Melt Index (g/10 min)	Maximum Drawdown (m/min.)	Neck-In 134 mpm/1 Mil (cm)	Output (kg/hr/hp)
1	A	None	4.5	183	21	3.2
13	A	LDPE	ND	549	9.9	3.5
14	A	EMA	ND	305	18.5	3.4
15	A	EAA	ND	219	17.3	3.5
16	B	LDPE	4.7	>610	9.9	3.8
17	C	LDPE	8.5	>610	9.9	4.4
18	M	LDPE	6.4	>610	12.7	3.7
19[a]	N	LDPE	ND	564	10.2	4.2
20*	F	LDPE	5.4	524	14.2	3.5

*Not an example of the present invention; provided for comparative purposes only.
[a]The blend combination of Sample N and sample O (Inventive Example 19) is extruded at a reduced extrusion melt temperature (270 C) due the high melt index of Inventive Sample N.
EMA = ethylene methyl acrylate copolymer comprised of 20 wt. percent methyl acrylate and having a 6 MI.
EAA = ethylene acrylic acid copolymer, supplied by The Dow Chemical Company as PRIMACOR™ 4608, comprised of 6.5 wt. percent acrylic acid and having an 8 MI.
LDPE = Sample O.
ND = not determined.

Table 9 shows blending minor amounts of a highly branched
ethylene polymer into a substantially linear ethylene polymer provides
extrusion compositions with excellent drawdown performance, lower neck-in
and improved specific output. Table 9 also show compositions comprised of
the substantially linear ethylene polymers of this invention are superior
to comparative linear ethylene polymer compositions, particularly with
respect to neck-in at higher drawdown rates. The ability to achieve less
neck-in at a higher drawdown rate, not only allows maximum
downgaugability, it also provides practitioners the advantage and
flexibility to lower the melt index to gain additional strength property
improvements.

EXAMPLE 21 - 27
In another extrusion coating evaluation, blends were prepared
using Inventive Sample M and comparative LDPE sample K as well as another
highly branched high pressure LDPE sample (comparative sample P).
Descriptions for Inventive Sample M and the LDPE sample P are listed in
Table 8. Using these polymers, extrusion coating compositions were
prepared dry-blending as described above in Examples 13-20 unless noted
otherwise. The compositions were evaluated on the Black Clawson extrusion
coater (described above) by increasing the take-off rate at constant screw
speed (90 rpms) and deducing the onset of draw resonance. As another part
of the evaluation, while being drawn at a constant 440 ft/min. (134
meter/min.), sheets of 0.5 mil oriented polypropylene (OPP) film were
slip-sheeted at the die to prepare extrusion laminates for adhesion
testing. Table 10 shows the blend composition sample descriptions and
extrusion melt temperatures as well as the drawdown, neck-in and OPP
adhesion performance for the various compositions evaluated. Inventive
Samples 23-27 employ Inventive Sample M.

Table 10

Example	Weight percent LDPE (Sample O)	Melt Temperature (C)	Maximum Drawdown (m/min.)	Neck-In at 134 mpm /1 Mil (cm)	OPP Adhesion (g/cm)
21*	100	330	268[a]	4.1	14.3
22*	100[tt]	332	271[a]	5.1	5.4
23	90	329	357	4.8	23.2
24	90[tt]	328	366	5.8	7.1
25	70	317	344	5.1	46.4
26	50	318	390	6.4	250
27	18	314	>610	12.7	>286

[t]Black Clawson coextrusion coater line is operated at a screw speed of 90 rpm for ~113 kg/hr.
*Not an example of the present invention; provided for comparative purposes only.
[a]Draw resonance was not observed; maximum drawdown deduced by melt tension breakage manifested as edge tears.
[tt]LDPE = Sample P instead of Sample O.

Figure 1 is a plot showing the maximum drawdown rate as a function of weight percent of a 6.7 Melt Index substantially linear ethylene polymer blended into a 8 Melt Index high pressure low density polyethylene where the blends comprise extrusion compositions. Surprisingly, Figure 1 together with Table 10 illustrate that these extrusion compositions show synergistic drawdown performance, that is, the drawdown rates of the combinations are higher than that of either polymer used alone. The synergistic performance and the discovery that the optimum or maximum drawdown performance occurs for compositions comprised of less than about 20 weight percent LDPE into at least one substantially linear polymer, is a contradistinction over the art provided by Kurtz et al. in US Patent 4,339,507 where LDPE blend combinations with a heterogeneous conventional linear ethylene polymer provide synergistic drawdown performance only when the composition is comprised of "greater than 20 weight percent and less than 98 weight percent of a high pressure LDPE" and, according to Figure 4 provided by Kurtz et al. in US Patent 4,339,507, the optimum amount of LDPE is about 45 - 50 weight percent for maximum synergistic drawdown performance. Moreover, on a percentage basis (which takes account of extrusion equipment differences), the apparent optimum illustrated in Figure 1 of this invention represents a more

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significant drawdown improvement or increase relative to the disclosed discoveries of Kurtz et al. Further, Table 10 also shows that the present inventive compositions provide exceptional and/or synergistic OPP adhesion when extrusion laminated or the like.

EXAMPLES 28 - 39: Ternary Polymer Blends

In the same manner as described for Examples 21-27, ternary blends were prepared using a substantially linear ethylene polymer, a linear ethylene polymer and a high pressure low density polyethylene polymer. The various blend combinations of these polymers is reported in Table 11. As dry-blended extrusion coating compositions, the polymer blends were evaluated on the Black Clawson extrusion as described in Example 5 to determine drawdown and neck-in performance. Resultant paper coatings and uncoated Kraft paper were also evaluated for tear resistance using the Elmendorf Tear method in accordance with ASTM D1938. The neck-in, drawdown rate before the onset of draw resonance and tear properties as well as polymer descriptions are all reported in Table 11.

Table 11

Ternary Polymer Blends

Example	LDPE (wt. percent)	ULDPE (wt. percent)	SLEP (wt. percent)	Neck-In 134 mpm/1 Mil (cm)	Maximum Drawdown (m/min.)	Tear Resistance (grams)[+]
28*	100	0	0	5.5	305	121
29*	20	80	0	10.9	>610	275
30*	80	20	0	4.8	380	134
31	80	0	20	4.8	450	134
32	20	0	80	10.9	>610	290
33	20	70	10	11.4	>610	253
34	20	50	30	11.7	>610	287
35	20	30	50	11.4	>610	276
36	70	20	10	5.3	405	155
37	50	20	30	6.1	415	298
38	30	20	50	8.4	>610	252
39[b]	0	0	0	NA	NA	92

*Not an example of the present invention; used for comparative purposes only.
SLEP = substantially linear ethylene polymer prepared by the interpolymerization of ethylene and 1-octene
      having a 8.1 Melt Index and a 0.913 g/cc density.
LDPE = traditional high pressure low density polyethylene; Comparative Sample O.
ULDPE = heterogeneous conventional ultra low linear low density olefin polymer of ethylene and 1-octene
      having a 6.0 Melt Index and a 0.911 g/cc density.
NA = not applicable.
[+]Tear resistance values are reported as (machine direction + transverse direction)/2.
[b]Sample 39 is uncoated Kraft paper and is not an example of the present invention.

        Table 11 shows that the ternary combination of substantially
linear ethylene polymers with high pressure polyethylene and linear
ethylene polymers can allow improved drawdown rates and improved tear
properties in comparison to high pressure polyethylene used alone in an
extrusion coating operation. Also, Table 11 shows that ternary blend
compositions based on substantially linear ethylene polymers offer better
overall performance attributes with respect to neck-in, drawdown and tear

properties when compared to known blend combinations involving high
pressure polyethylene and heterogeneous conventional linear ethylene
polymers.

5   FIGURE 2: Melt Elasticity

          In another experiment, the relative melt tension or melt
elasticity of inventive blends and heterogeneous conventional blend
compositions was determined. The experiment involved two substantially
linear ethylene polymers, one heterogeneous linear low density
10   polyethylene and one high pressure low density polyethylene. The property
descriptions of these raw materials are listed in Table 12. Melt blends
of the substantially linear ethylene polymers with LDPE and a blend of
LLDPE with LDPE were prepared by melt mixing the components in a Haake
Rheocorder mixer at a 160 C melt temperature and 40-60 rpm rotor speed for
15   a total of five minutes. The resultant blends were granulated and
compression molded into 3 mm thick plates for melt elasticity testing.
The pure components (base polymers) were also subjected to identical Haake
mixer treatment. The melt index (I_2) and melt tension were determined for
the resultant blends and pure components as described above. The melt
20   elasticity was determined by using a Rheometrics Dynamic Analyzer II where
the dynamic shear viscosity experiment was performed from 0.05 Hz to 100
Hz under 15 percent strain at 160 C and the melt viscosity at zero shear
rate was interpolated from the resultant plot. Table 13 shows the melt
index, melt tension and zero shear viscosity for the three polymer blends.
25   Figure 2 is a plot of zero shear melt viscosity as a function of weight
percent high pressure low density polyethylene in the blend. These data
show that polymer blends involving a substantially linear ethylene
homopolymer and copolymer exhibit synergistic melt elasticity behavior
(opposed to linear or directly additive behavior) as measured by zero
30   shear viscosity which represents the unperturbed chain entanglement
capability. Higher zero shear viscosity and chain entanglement
capability, which is the origin of melt strength, is thought to relate
directly with long chain branching and allows for the build up of melt
stress during high shear drawing at high line speeds.
35

Table 12

Polymer Blend Raw Materials

Sample	Polymer Type	Melt Index, I_2 (g/10 min)	Density (g/cc)	Melt Tension (grams)	I_{10}/I_2
Q	SLEP	1.03	0.9192	1.9	9.4
R	SLEP[+]	0.97	0.9512	3.0	12.1
S*	LINEAR	1.0	0.920	1.2	8.0
T*	LDPE	0.7	0.923	9.8	9.8

*Not an example of the present invention when used alone.
SLEP = substantially linear ethylene polymer prepared by the interpolymerization of ethylene with 1-octene.
[+]SLEP = substantially linear ethylene polymer prepared by the homopolymerization of ethylene.
LDPE = traditional high pressure low density polyethylene.
LINEAR = heterogeneously linear low density polyethylene prepared by the interpolymerization of ethylene
    with 1-octene; supplied by The Dow Chemical Company under the trademark of DOWLEX™ 2045.
ND = not determined.

Table 13

Example	Base Polymer (Sample #)	percent LDPE (Sample T)	Melt Index (g/10 min.)	Melt Tension (grams)	Zero Shear Viscosity (X e^5 poise)
	Melt Elasticity of Haake-Mixed Polymer Blends				
40*	T	100	14.08	12.63	3.6
41	Q	80	13.08	11.56	3.5
42	Q	65	12.19	11.45	3.41
43	Q	50	10.54	10.93	3.15
44	Q	30	3.89	10.24	2.83
45	Q	10	2.36	9.71	2.2
46	Q	0	3.65	9.21	1.93
47*	T	100	ND	ND	3.6
48*	S	95	ND	ND	2.76
49*	S	85	ND	ND	2.66
50*	S	70	ND	ND	2.6
51*	S	30	ND	ND	1.99
52*	S	0	ND	ND	1.26
53*	T	100	13.79	11.8	3.6
54	R	90	16.96	13.34	3.52
55	R	80	14.65	13.33	3.47
56	R	50	11.11	13.13	3.31
57	R	20	6.74	14.13	2.87
58	R	0	3.01	13.01	1.9

*Not an example of the present invention; provided for comparative purposes.
ND = not determined.

EXAMPLES 59-65:   Molecular Interrelationships

In another extrusion coating evaluation, draw ratio was approximated from web thicknesses. The molecular interrelationship between melt index, melt tension and maximum draw ratio before the onset of draw resonance was elucidated by performing standard least squares

regression analysis on the dataset shown in Table 14. The following equation shows the interrelationship:

$$\text{Critical Draw Ratio} = a * MT - b * MI - c * MT^2 + d * MI^2 + e * MT * MI$$

where,

a is a coefficient from 39 to 60, and especially from 45 to 53; b is a coefficient from 7 to 11, and especially from 8 to 10.5; c is a coefficient from 33 to 46, and especially from 36 to 43; d is a coefficient from 0.5 to 0.9, and especially from 0.55 to 0.85; e is a coefficient from 13 to 24, and especially from 16 to 21; MT is Melt Tension determined at 190 C as described above; and MI is Melt Index determined in accordance with ASTM D1238 Condition 190 C/2.16 kg.

Table 14

Molecular Interrelationships

Example	Blend Component(s)	Component Weight percent	Melt Index (g/10 min)	Melt Tension (grams)	Draw Ratio
59	Sample A	100	4.5	0.46	28
60	Sample B	100	4.7	0.53	31
61	Sample C	100	9.4	0.28	35
62*	Sample O	100	7.9	4.48	49
63	Sample A/O	90/10	4.9	0.88	65
64	Sample B/O	90/10	4.45	0.91	61
65	Sample A/O	70/30	4.8	1.9	92

*Not an example of the present invention when used alone.

CLAIMS

1.   In a process for extrusion coating a substrate or for making a cast film with a thermoplastic composition, comprising the steps of:

(i)   feeding a thermoplastic composition into at least
       one extruder,

(ii)   melting and mixing the thermoplastic composition to form
       at least one uniform molten polymer stream,

(iii) extruding the molten polymer stream through a die to
       form a primary web,

the improvement comprising:

(i)   operating said extruder at line speeds greater than 152
       meters/minute, and either

       (a)   drawing down said web onto said substrate to
       thereby coat said substrate with at least one layer of
       said thermoplastic composition, or

       (b)   cooling and drawing down said web onto a take-off
       device to make said film with at least one layer of said
       thermoplastic composition,

(ii)   transporting or collecting said coated substrate or
       said film for subsequent use, and

(iii) using as said thermoplastic composition:

       (I)   from 10 to 100 percent by weight of at least one
       substantially linear ethylene polymer characterized as
       having:

              (a)   a melt flow ratio, I_{10}/I_2, $\geq$ 5.63,

              (b)   a molecular weight distribution, M_w/M_n,
                     defined by the equation:
                     $M_w/M_n \leq (I_{10}/I_2) - 4.63$,

              (c)   a critical shear rate at the onset of surface
                     melt fracture of at least 50 percent greater
                     than the critical shear rate at the onset of
                     surface melt fracture of a linear olefin
                     polymer having about the same I_2 and
                     M_w/M_n, and

(d) a single melting peak as determined using
     differential scanning calorimetry;
     and

(II) from 0 to 90 percent by weight of at least
     one polymer selected from the group consisting of
     a heterogeneous linear ethylene polymer and high
     pressure ethylene polymer.

2.   The process defined in Claim 1 wherein (I) is an
ethylene homopolymer.

3.   The process defined in Claim 1 wherein (I) is an
interpolymer of ethylene and at least one C_3-C_{20} α-olefin.

4.   The process defined in Claim 1 wherein (I) is a
copolymer of ethylene and one C_3-C_{20} α-olefin.

5.   The process defined in Claim 1 wherein (I) is a terpolymer
of ethylene and two C_3-C_{20} α-olefins.

6.   The process defined in Claim 1 wherein the Dow Rheology
Index (DRI) of (I) is at least 0.1.

7.   The process defined in Claim 1 wherein (I) has a melt
index, I_2, from 1 grams/10 minutes to 10 grams/10 minutes, a density from
0.9 grams/cm^3 to 0.94 grams/cm^3, a molecular weight distribution, M_w/M_n,
from 1.5 to 6.5, a melt flow ratio, I_{10}/I_2, of 8 to 12, a DRI of at least
0.1, and a draw ratio of at least about 18.

8.   The process defined in Claim 1 wherein (II) is an
interpolymer of ethylene and at least one C_3-C_{20} α-olefin.

9.   The process defined in Claim 1 wherein (II) is a
copolymer of ethylene and one C_3-C_{20} α-olefin.

10.   The process defined in Claim 1 wherein (II) is linear low density polyethylene.

11.   The process defined in Claim 1 wherein (II) is ultra low density polyethylene.

12.   The process defined in Claim 1 wherein (II) is low density polyethylene.

13.   The process defined in Claim 1 wherein (II) is an interpolymer of ethylene and at least one α,β-ethylenically unsaturated comonomer.

14.   The process defined in Claim 1 wherein (II) is a copolymer of ethylene and one α,β-ethylenically unsaturated comonomer.

15.   The process defined in Claim 1 wherein (II) is a copolymer of ethylene with acrylic acid.

16.   The process defined in Claim 1 wherein (II) is a copolymer ethylene with methyl acrylate.

17.   The process defined in Claim 1 wherein (II) is at least one high pressure ethylene polymer.

18.   The process defined in Claim 1 wherein (II) is at least one linear ethylene polymer.

19.   The process defined in Claim 1 wherein said composition is a ternary blend comprising at least one substantially linear ethylene polymer and at least one high pressure ethylene polymer and at least one linear ethylene polymer.
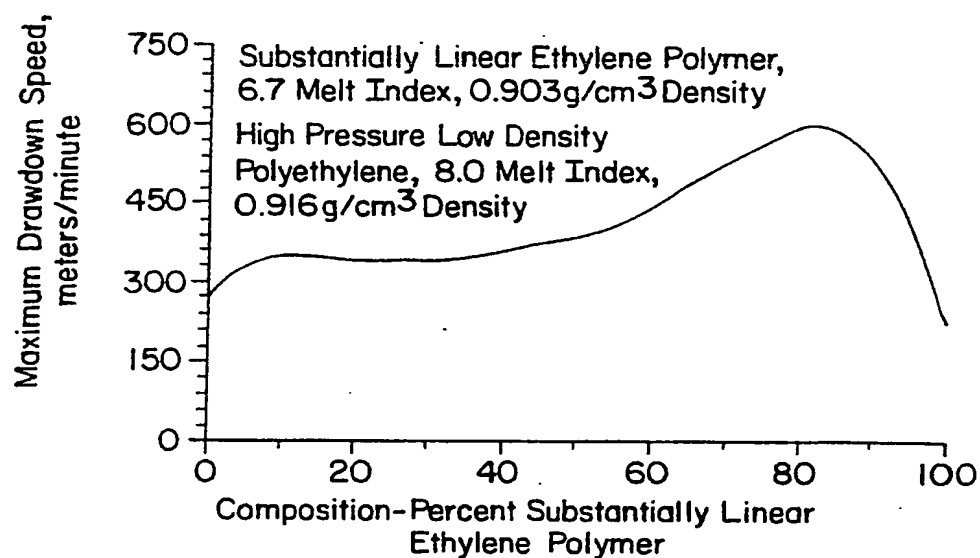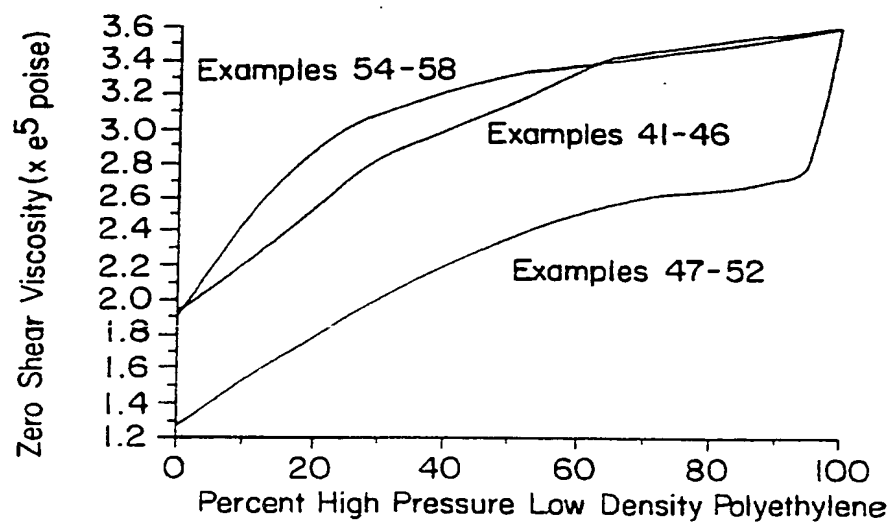
FIG. 1

Substantially Linear Ethylene Polymer, 6.7 Melt Index, 0.903g/cm^3 Density

High Pressure Low Density Polyethylene, 8.0 Melt Index, 0.916g/cm^3 Density

FIG. 2

Examples 54-58

Examples 41-46

Examples 47-52

Interr   nal Application No
PCT/US 94/06325

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   B29C47/00   B32B31/30   B29D7/00   B29D9/00   //B29K23:00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   B29C   B32B   B29D   C08F   C08L   C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category°	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO,A,94 06857 (EXXON CHEMICAL PATENTS INC.) 31 March 1994 see page 7, line 13 - line 16 see page 8, line 23 - line 35; claims 1-3; example 1 ---	1-9, 12-16
Y	WO,A,93 08221 (THE DOW CHEMICAL COMPANY) 29 April 1993 cited in the application see page 30, line 1 - page 32, line 11 see page 33, line 12 - line 15 see page 33, last paragraph - page 34, paragraph 3; claims 2,7,9,10,25,26 ---	1-19
Y	EP,A,0 292 336 (THE DOW CHEMICAL COMPANY) 23 November 1988 cited in the application see claims 1,4 ---	1-19

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| X | Further documents are listed in the continuation of box C. | | X | Patent family members are listed in annex. |

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Date of the actual completion of the international search

14 November 1994

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Form PCT/ISA/210 (continuation of second sheet) (July 1992)

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